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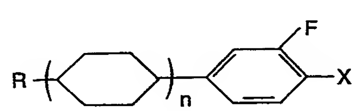
(54) Fluorobenzene derivatives and liquid crystal compositions containing the same.

(57) Fluorobenzene derivatives expressed by the general formula



wherein n represents 1 or 2, X represents CN or $COCH_3$, and R represents a hydrogen atom or an alkyl or alkoxy group each of 1 to 15 carbon atoms are liquid crystal compounds having a large positive dielectric anisotropy value and also a low viscosity and a good stability to heat, light, air and water, and are suited for use in liquid crystal compositions.

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FLUOROBENZENE DERIVATIVES AND LIQUID CRYSTAL COMPOSITIONS CONTAINING THE SAME

This invention relates to novel liquid crystal compounds having a positive dielectric anisotropy, and liquid crystal compositions containing the same.

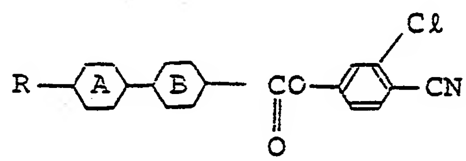
Liquid crystal display elements utilize the optical anisotropy and dielectric anisotropy of liquid crystal substances, and are classified into various types such as TN (twisted nematic) type, DS (dynamic scattering) type, guest-host type, DAP type, White-Tailor type, etc according to their display modes. The properties required of the liquid crystal substances for their respective uses are different. For example, liquid crystal substances having a positive dielectric anisotropy $\Delta\varepsilon$ might be required or one having a negative one are required or one having an intermediate value, depending on the kind of display elements. Anyhow, however, in any mode, the liquid crystal substances have to exhibit a liquid crystal phase in temperature ranges as broad as possible, around room temperature, and also have to be stable to heat, air, light, etc. At present, however, there is no single compound which alone satisfies all such conditions. It is the present state of the art that several kinds of liquid crystal

compounds or such compounds and non-liquid crystalline compounds are mixed to obtain a mix which will meet current practical uses.

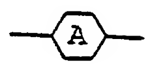
Recently, the need particularly for liquid crystal display elements which can be driven at low voltages has increased, and in order to satisfy such a requirement, liquid crystal compositions having a larger $\Delta\varepsilon$ value are usually required.

In general, liquid crystal compositions having a desired $\Delta\varepsilon$ value can be obtained by adequately mixing compounds having a positive $\Delta\varepsilon$ value with those having a negative $\Delta\varepsilon$ value. Thus, in order to obtain a liquid crystal composition having a large positive $\Delta\varepsilon$ value, a component having as large a positive $\Delta\varepsilon$ value as possible will have be to be used. In this case, however, the component will still have to have a good compatibility with other components and extend the mesomorphic range of the resulting composition or at least not narrow it.

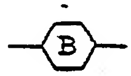
In order to satisfy such an object, we have described in Japanese patent application laid-open No Sho 57-154158/1982 a series of carboxylic acid 3-chloro-4-cyanophenyl esters expressed by the general formula



wherein R' represents an alkyl group or alkoxy group of 1 to 10 carbon atoms and



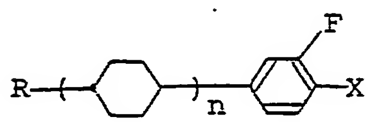
and



represents a benzene or cyclohexane ring.

Liquid crystal display elements having a higher level of performances continue to be needed, and compounds having a lower viscosity and a good stability to heat, light, air and moisture have been required. The present invention has been made to meet such a demand.

The present invention resides in flurorobenzene derivatives expressed by the general formula

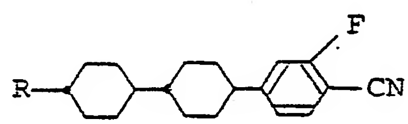


(I)

wherein n represents 1 or 2; X represents CN or $COCH_3$; and R represents hydrogen or an alkyl or alkoxy group of 1 to 15 carbon atoms. The present invention also provides liquid crystal compositions containing the compounds.

In particular, compounds of the above general formula wherein X represents CN have a positive dielectric anisotropy value typically as large as about +30, a low viscosity for such a value and a good stability to heat, light, air and water and exhibit a liquid crystal phase in broad temperture range; hence they are suitable as components constituting a liquid crystal composition which has a large $\Delta\varepsilon$ value, a low viscosity and a broad mesomorphic range.

More particularly, compounds of the general formula wherein X represents CN and n is 2, that is, 3-fluoro-4-cyano-1-[*trans*-4-(*trans*-4-substituted cyclohexyl)cyclohexyl]benzenes expressed by the general formula



(II)

wherein R is as defined above, exhibit a liquid crystal phase within a broad mesomorphic range up to high temperatures. Furthermore, compounds of the formula (I) wherein X represents $COCH_3$ have a low viscosity although their $\Delta\varepsilon$ values are small. Particularly, compounds of the formula (I) wherein X represents $COCh_3$ and n is 2 exhibit a liquid crystal phase in a broad temperature range. Such compounds of the formula (I) wherein X represents $COCH_3$ can be obtained as intermediate compounds in the preparation of compounds of the formula (I) wherein X represents CN.

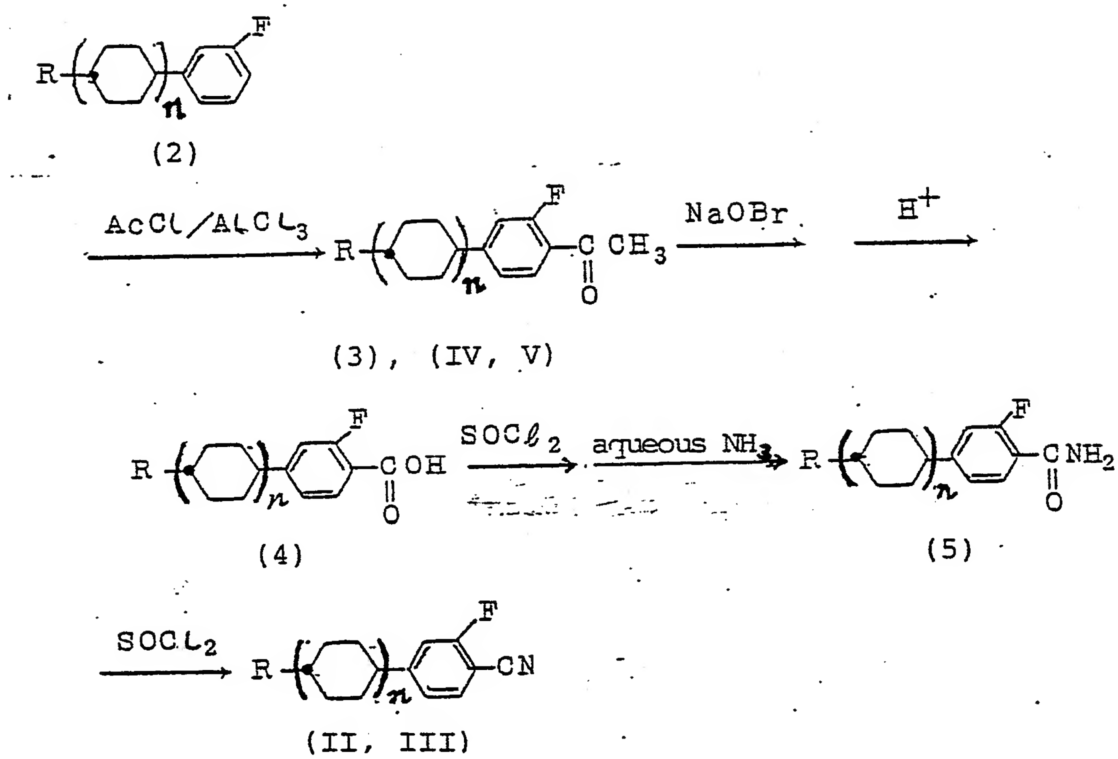
The present invention also provides a process for preparing the compounds of formula (I). In the process, a 1-fluoro-3-(4-substituted cyclohexyl)benzene corresponding to a compound of formula (I) which has hydrogen in place of the substituent X, is acetylated to

give a compound of formula (I) where X is $COCH_3$, and the $COCH_3$ group is optionally converted to a nitrile group.

Aspects of the process will now be described in more detail, referring to the following reaction scheme:

A 1-fluoro-3-(4-substituted cyclohexyl)benzene (a compound of the formula (2) wherein _n_ is 1) or a 1-fluoro-3-[_trans_-4-(_trans_-4-substituted cyclohexyl)-cyclohexyl]benzene (a compound of the formula (2) wherein _n_ is 2), can be prepared according to a known method (for example, the method described in USP 4405488), and is preferably reacted with acetyl chloride in the presence of aluminium chloride using CS_2 as solvent to obtain a 2-fluoroacetophenone derivative (3) corresponding to the formulae (IV) and (V) of the claimed compounds. This derivative can then be reacted for instance with sodium hypobromite in dioxane to obtain a carboxylic acid compound (4) which may be reacted with thionyl chloride in toluene to obtain an acid chloride compound, which in turn may then be reacted with aqueous ammonia to obtain an acid amide compound (5) and then dehydrated with thionyl chloride to obtain the desired 3-fluoro-4-cyano-1-(_trans_-4-substituted cyclohexyl)benzene (III) or 3-fluoro-4-cyano-1-[_trans_-4'-(_trans_-4-substituted cyclohexyl)cyclohexyl]benzene (II).

The foregoing is illustrated by the following chemical formulas:



The present invention will be further described in detail by way of Examples.

Example 1

Preparation of 2-fluoro-4-(trans-4-heptylcyclohexyl)-acetophenone (a compound of the formula (I) wherein X represents $COCH_3$ and n is 1, i.e. a compound of the formula (V) wherein R represents C_7H_{15}).

1-Fluoro-3-(4-heptylcyclohexyl)benzene (18 g) was dissolved in CS_2 (50 mℓ), and aluminum chloride (7.2 g) was then dissolved in the solution, followed by adding acetyl chloride (5.3 g) with stirring at 2 to 5°C for 10 minutes, gradually raising the temperature up to 35°C, keeping this temperature for 2 hours, cooling the mixture, adding 6N hydrochloric acid (50 mℓ), subjecting the resulting oil layer to extraction with toluene (100 mℓ), washing the solution with water till the washing liquid became neutral, distilling off the solvent under reduced pressure and recrystallizing the residue from ethanol to obtain the objective 2-fluoro-4-(trans-4-heptylcyclohexyl)acetophenone (yield: 9 g). This product was of a monotropic liquid crystal and exhibited a melting point (C-I point) of 35.6 ~ 40.2°C and a nematic-clearing point (N-I point) of 21.5°C.

The following compounds were prepared in the same manner as above:

2-fluoro-4-(trans-4-propylcyclohexyl)acetophenone
m.p. 63.3 ~ 64.7°C

2-fluoro-4-(trans-4-butylcyclohexyl)acetophenone
m.p. 73 ~ 77°C

2-fluoro-4-(trans-4-pentylcyclohexyl)acetophenone
m.p. 10.1 ~ 13.5°C

2-fluoro-4-(trans-4-hexylcyclohexyl)acetophenone

m.p. 58.2 ~ 62.2°C

N—I point 12.9°C

Example 2 Preparation of 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)-benzene (a compound of the formula (I) wherein X represents CN and n is 1, i.e. a compound of the formula (III) wherein R represents C_7H_{15})

Crystals of 2-fluoro-4-(trans-4-heptylcyclohexyl)-acetophenone obtained in Example 1 (15 g) were dissolved in dioxane (50 mℓ) and cooled down to 10°C or lower. Separately, sodium hydroxide (40 g) was dissolved in ice water (200 mℓ), and bromine (40 g) was dropwise added to the solution to obtain a solution of sodium hypobromite. This solution was dropwise added with stirring to the solution of the above compound, while keeping the temperature at 10°C or lower, warming the mixture to 35°C over 3 hours, allowing to stand overnight, adding 6N-hydrochloric acid (100 mℓ) for acidification, filtering the mixture to recover the precipitate and recrystallizing it from acetic acid (20 mℓ) to obtain crystals of 2-fluoro-4-(trans-4-heptylcyclohexyl)benzoic acid (4).

Crystals of this compound (4) (12 g) were suspended in toluene (20 mℓ), followed by adding thionyl chloride (5.9 g) to the suspension, reacting them at 70°C for

6 hours, distilling off excess thionyl chloride under reduced pressure, pouring a residual oily substance in an aqueous ammonia (50 mℓ), recovering the resulting precipitate by filtration, and recrystallizing it from toluene to obtain crystals of 2-fluoro-4-(trans-4-heptylcyclohexyl)benzoic acid amide (5). The crystals (1.5 g) were dissolved in a mixture of toluene (50 mℓ) with dimethylformamide (50 mℓ), followed by adding thionyl chloride (5 g), subjecting the mixture to dehydration reaction at 80°C for 5 hours, cooling the resulting material, adding ice water (50 mℓ), subjecting it to extraction with toluene (200 mℓ), distilling off the resulting oily substance under reduced pressure, filtering off insoluble matters, putting the filtrate in a refrigerator for crystallization, and recrystallizing the resulting crystals from n-heptane to obtain crystals of 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)benzene (yield; 0.2 g). The crystals exhibited a C-N point of 19.6 ~ 20.9°C and a N-I point of 21.2°C.

Compounds of the formula (III) containing other substituents were obtained in the same manner as above.

Example 3

Preparation of 4-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone (a compound of the formula (I) wherein X represents $COCH_3$ and n is 2, i.e. a compound of the formula (IV) wherein R represents C_3H_7

3-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]fluorobenzene (5 g) was dissolved in CS_2 (50 mℓ), followed by adding aluminum chloride (4 g), dropwise adding acetyl chloride (3 g) with stirring at 5°C or lower, raising the temperature up to 35°C, agitating the mixture for 2 hours, adding cold hydrochloric acid, subjecting the resulting precipitate to filtration and washing with ice water, and recrystallizing it from a mixed solvent of acetone with toluene to obtain the objective 4-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone (yield: 18%). It exhibited a C-N point of 88 ~ 90°C and a N-I point of 293°C.

4-[Trans-4-(trans-4-butylcyclohexyl)cyclohexyl]-2-fluoroacetophenone was obtained in the same manner as above. It exhibited a C-N point of 50 ~ 53.5°C and a N-I point of 123°C.

Example 4

Preparation of 3-fluoro-4-cyano-1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene (a compound of the formula (I) wherein X represents CN and n is 2, i.e. a compound of the formula (II) wherein R represents C_3H_7)

4-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone (0.7 g) was suspended in dioxane (50 mℓ), followed by keeping the suspension at 10°C or lower, dropwise adding to it with stirring, a solution of sodium hypobromite prepared by adding bromine (1.6 g) to sodium hydroxide (2 g) and ice water (30 mℓ), raising the temperature up to 35°C, continuing agitation for 5 hours, cooling the resulting material, acidifying it with 6N-hydrochloric acid, and subjecting the precipitate to filtration and water-washing to obtain 4-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-fluorobenzoic acid, which was then recrystallized from acetic acid and dried. The product (0.6 g) was dissolved in toluene (20 mℓ), followed by adding thionyl chloride (2 g), refluxing the mixture for 3 hours, distilling off excess thionyl chloride under reduced pressure, pouring the resulting residual oily substance in an aqueous ammonia, filtering and water-washing the resulting

precipitate, and recrystallizing it from toluene to obtain 4-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-fluorobenzoic acid amide. This product (0.4 g) was dissolved in dimethylformamide (10 mℓ) and toluene (10 mℓ), followed by adding thionyl chloride (2 g), refluxing the mixture for 4 hours, cooling it, adding cold water, subjecting the mixture to separation and extraction with toluene (50 mℓ), water-washing the resulting oily layer till the washing liquid became neutral, distilling off toluene under reduced pressure, and recrystallizing a remaining oily substance from a mixed solvent of toluene with acetone to obtain crystals of the objective 3-fluoro-4-cyano-1-[trans-4-propylcyclohexyl)cyclohexyl]benzene (yield: 0.1 g). This product exhibited a crystalline-smectic point of 53.8°C; a smectic-nematic point of 89.8°C and a nematic-clearing point of 207°C.

3-Fluoro-4-cyano-1-[trans-4-(trans-4-substituted cyclohexyl)cyclohexyl]benzenes having other substituents were obtained in the same manner as above.

<u>Use example 1</u>

A liquid crystal composition (A) consisting of

trans-4-propyl-(4'-cyanophenyl)cyclohexane
24% by weight,

trans-4-pentyl-(4'-cyanophenyl)cyclohexane
36% by weight,

trans-4-heptyl-(4'-cyanophenyl)cyclohexane

25% by weight, and

trans-4-pentyl-(4"-cyanobiphenyl)cyclohexane

15% by weight,

had a nematic temperature range of -10°C ~ +72.1°C and a viscosity at 20°C of 28 cp. When the composition was sealed in a TN cell having a transparent electrode and a distance between the inner walls, of 10 μm, the cell exhibited a threshold voltage of 1.76 V and a saturation voltage of 2.40 V.

2-Fluoro-4-(trans-4-heptylcyclohexyl)acetophenone of Example 1 (5 parts by weight) was added to the above liquid crystal composition (A) (95 parts by weight). The resulting liquid crystal composition had a N-I point of 68.4°C, but its viscosity at 20°C was 27 cp and when it was sealed in the above TN cell, the threshold voltage and the saturation voltage were 1.69 V and 2.32 V, respectively.

Use example 2

A liquid crystal composition consisting of the above liquid crystal composition (A) (90% by weight) and 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)-benzene of Example 2 (10% by weight) had a N-I point of 66.3°C, a viscosity at 20°C of 27 cp and a $\Delta\varepsilon$ of 13.4, and when it was sealed in the above cell, the threshold voltage

and the saturation voltage were 1.62 V and 2.24 V, respectively.

Use example 3

A liquid crystal composition (B) consisting of

trans-4-propyl-(4'-cyanophenyl)cyclohexane
28 by weight,

trans-4-pentyl-(4'-cyanophenyl)cyclohexane
42% by weight and

trans-4-heptyl-(4'-cyanophenyl)cyclohexane
30% by weight,

exhibited a nematic temperature range of −3°C ~ +52°C. The threshold voltage, the saturation voltage and the viscosity at 20°C were 1.6 V, 2.2 V and 23 cp, respectively.

4-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone of Example 3 (10 parts by weight) was added to the above liquid crystal composition (B) (90 parts by weight). The resulting liquid crystal composition exhibited a N-I point of 62°C, and its viscosity at 20°C was 24 cp, i.e. almost unchanged.

Thus, when the compound of the present invention was added, it was possible to obtain a liquid crystal composition having a low viscosity and a high clearing point.

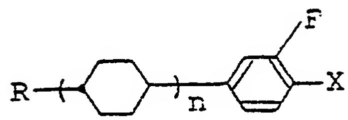
Use example 4

A liquid crystal composition consisting of the above liquid crystal compostion (B) (90 parts by weight) and 3-fluoro-4-cyano-1-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]benzene of Example 4 (10 parts by weight) had a N-I point of 66°C and a $\Delta\varepsilon$ of +12.5, and when a TN cell was prepared in the same manner as above, the threshold voltage and the saturation voltage lowered down to 1.40 V and 1.90 V, respectively, and the viscosity increased up to 29 cp, but such an extent of value is not practically a hindrance.

As described above, when the compound of the present invention is used, it is possible to reduce the operation voltage of display elements and also to broaden their operation temperature range.

CLAIMS

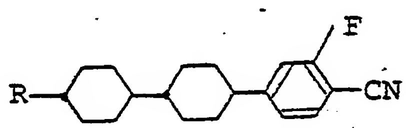
1. A flurobenzene derivative expressed by the general formula



(I)

wherein n represents 1 or 2, X represents CN or $COCH_3$ and R represents a hydrogen atom or an alkyl or alkoxy group of 1 to 15 carbon atoms.

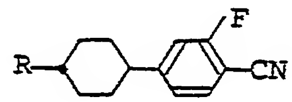
2. A 3-fluoro-4-cyano-1-[trans-4-(trans-4-substituted cyclohexyl)cyclohexyl]benzene expressed by the general formula



(II)

wherein R represents a hydrogen atom or an alkyl or alkoxy group of 1 to 15 carbon atoms.

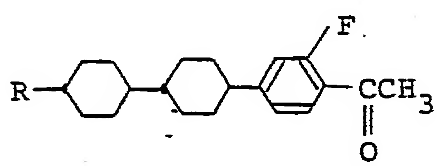
3. A 3-fluoro-4-cyano-1-(trans-4-substituted cyclohexyl)benzene expressed by the general formula



(III)

wherein R represents an alkyl or alkoxy group of 1 to 15 carbon atoms.

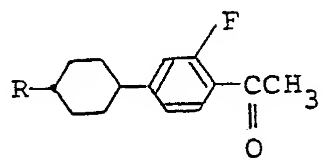
4. A 4-[trans-4-(trans-4-substituted cyclohexyl)-cyclohexyl]acetophenone expressed by the general formula



(IV)

wherein R represents an alkyl or alkoxy group of 1 to 10 carbon atoms.

5. A 4-(trans-4-substituted cyclohexyl)acetophenone expressed by the general formula



(V)

wherein R represents an alkyl or alkoxy group of 1 to 10 carbon atoms.

6. A liquid crystal composition contaning at least one fluorobenzene derivative as defined in any preceding claim.

7. A process for preparing a compound of formula (I), as defined in claim 1, wherein a 1-fluoro-3-(4-substituted cyclohexyl)benzene corresponding to a compound of formula (I) which has hydrogen in place of the substituent X, is acetylated to give a compound of formula (I) where X is $COCH_3$, and the $COCH_3$ group is optionally converted to a nitrile group.

European Patent Office

0119756

Application number

EUROPEAN SEARCH REPORT

EP 84301072.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
P,X	EP - A1 - 0 090 183 (MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG * Claims 1,4 * --	1-6	C 07 C 121/60 C 07 C 121/75 C 07 C 120/00 C 07 C 49/813 C 07 C 49/84 C 07 C 45/46 C 09 K 3/34
A	DE - A1 - 3 223 637 (CHISSO CORP.) * Claims 1,4; pages 8,9 * --	1-3,6, 7	
A	DE - A1 - 2 918 775 (MERCK PATENT GMBH) * Claims 1,2,7,8 * --	1,5,6	
A	GB - A - 2 090 593 (HOFFMANN - LA ROCHE & CO. AKTIENGESELLSCHAFT) * Claims 1,14,15 * ----	1,4,6, 7	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 07 C 49/00 C 07 C 121/00 C 09 K 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-05-1984	HOFBAUER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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